

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 July 2003 (10.07.2003)

PCT

(10) International Publication Number
WO 03/056100 A1

(51) International Patent Classification⁷: **D21H 17/71**,
17/68, 21/10

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(21) International Application Number: **PCT/SE02/02443**

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date:
20 December 2002 (20.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01850225.2 21 December 2001 (21.12.2001) EP

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **AQUEOUS SILICA-CONTAINING COMPOSITION AND PROCESS FOR PRODUCTION OF PAPER**

(57) Abstract: The present invention refers to a process for the production of paper from a suspension containing cellulosic fibres, and optionally fillers, comprising adding to the suspension at least one cationic organic polymer and an aqueous silica-containing composition comprising an anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles, the composition having a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles within the range of from 0.2:1 to 99:1, and containing naphthalene sulphonate formaldehyde condensate and silica-based particles in an amount of at least 0.01 % by weight, based on the total weight of the aqueous silica-containing composition, and with the proviso that the composition contains substantially no cellulose-reactive sizing agent. The invention also encompasses an aqueous silica-containing composition and a method for preparation of an aqueous silica-containing composition.

Aqueous silica-containing composition and process for production of paper

The present invention relates to a process for the production of paper from a suspension containing cellulosic fibres, comprising adding at least one cationic organic polymer and an aqueous silica-containing composition comprising an anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles. The invention further relates to an aqueous silica-containing composition and methods for the preparation of the aqueous silica-containing composition, and uses of the aqueous silica-containing composition.

Background of the Invention

In the papermaking art, an aqueous suspension containing cellulosic fibres, and optionally fillers and additives, referred to as stock, is fed into a headbox which ejects the stock onto a forming wire. Water is drained from the stock through the forming wire, so that a wet web of paper is formed and dewatered on the wire. The paper web is then dried in the drying section of the paper machine. Drainage and retention aids are conventionally introduced into the stock in order to facilitate drainage and to increase adsorption of fine particles onto the cellulosic fibres to retain them with the fibres on the wire.

US 4,388,150 discloses a binder in papermaking comprising a complex of cationic starch and colloidal silicic acid to produce a paper having increased strength and improved levels of retention of added minerals and papermaking fines.

US 4,750,974 discloses a coarcervate binder for use in papermaking comprising a tertiary combination of a cationic starch, an anionic high molecular weight polymer and a dispersed silica.

US 5,368,833 discloses silica sols containing aluminium modified silica particles with high specific surface area and a high content of microgel.

US 6,083,997 discloses anionic nano-composites, which are prepared by adding a polyelectrolyte to silicate solution and then combining them with silicic acid. The nano-composites exhibit retention and drainage performance in papermaking.

EP 0 418 015 A1 discloses an active sizing composition containing an aqueous emulsion in combination with an anionic dispersant or emulsifier. By using anionic polyacrylamide, anionic starch or colloidal silica the anionic charge density in the sizing composition can be extended.

US 4,443,496 refers to a method for modifying a surface layer of hardened cement or substrates with use of the agent which comprises in a specified ratio of an alkali silicate solution and a sodium naphthalene sulphonate formaldehyde condensate.

US 4,559,241 relates to an aqueous solution of alkali metal silicate and nitrite.

The solution may also contain additives such as formaldehyde condensate with naphthalene sulphonate.

US 5,595,629 refers to a papermaking process comprising adding to the slurry an anionic polymer and cationic polymer in order to increase retention and/or dewatering.

- 5 The anionic polymer comprises a formaldehyde condensate of naphthalene sulfonic acid salt with a molecular weight range of 500 to 120,000.

US 6,033,524 discloses a method for increasing retention and drainage of filling components in a paper making furnish in a paper making process comprising adding to the furnish a slurry of filling components, also containing a phenolic enhancer.

- 10 US 4,772,332 pertains to a heat stabilised slurry of bulked kaolin pigment which is prepared by mixing a water soluble cationic material with kaolin clay pigment in the presence of water.

- US 5,733,414 relates to a process for manufacturing paper from a cellulosic suspension comprising adding a water soluble cationic polymer and a water soluble
15 formaldehyde condensate resin.

US 5,110,414 discloses a procedure for manufacturing lignocellulosic material products and improving their strength and water resistant characteristics, high molar mass lignin derivatives being added to the material.

- It would be advantageous to be able to provide drainage and retention aids with
20 improved performance. It would also be advantageous to be able to provide retention and drainage aids with good storage stability. It would further be advantageous to be able to provide a papermaking process with improved drainage and/or retention performance.

The Invention

- 25 According to the present invention it has unexpectedly been found that an improved drainage and/or retention effect of a cellulosic suspension on a wire can be obtained by using an aqueous silica-containing composition comprising anionic naphthalene sulphonate formaldehyde condensate and silica-based particles. The present invention makes it possible to increase the speed of the paper machine and to
30 use a lower dosage of additives to give a corresponding drainage and/or retention effect, thereby leading to an improved papermaking process and economic benefits.

- The terms "drainage and retention aid", as used herein, refer to one or more components, which when added to an aqueous cellulosic suspension, give better drainage and/or retention than obtained when not adding the said one or more
35 components. All types of stocks, in particular stocks having high contents of salts (high conductivity) and colloidal substances will obtain better drainage and retention performances by the addition of the composition according to the present invention.

Improved drainage and retention performances are important in papermaking processes for instance in processes with a high degree of white water closure, i.e. extensive white water recycling and limited fresh water supply.

In accordance with the present invention there is provided a process for the production of paper from a suspension containing cellulosic fibres, and optionally fillers, comprising adding to the suspension at least one cationic organic polymer and an aqueous silica-containing composition comprising an anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles, the composition having a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles, calculated as SiO_2 , within the range of from 0.2:1 to 99:1, and containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight, based on the total weight of the aqueous silica-containing composition, and with the proviso that the composition contains substantially no cellulose-reactive sizing agent.

There is further provided an aqueous silica-containing composition comprising an anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles comprising aggregated or microgel formed silica-based particles, the composition having a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles, calculated as SiO_2 , within the range of from 0.2:1 to 99:1, and containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight, based on the total weight of the aqueous silica-containing composition, and with the proviso that the composition contains substantially no cellulose-reactive sizing agent.

There is further provided an aqueous silica-containing composition obtainable by mixing anionic naphthalene sulphonate formaldehyde condensate with an aqueous alkali stabilised silica-based sol having an S-value in the range of from about 5 up to about 50% containing anionic aggregated or microgel formed silica-based particles, to provide an aqueous silica-containing composition containing an anionic naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight, based on the total weight of the aqueous silica-containing composition, with the proviso that the aqueous silica-containing composition contains substantially no cellulose-reactive sizing agent.

There is further provided a method for preparation of an aqueous silica-containing composition, which comprises mixing in the presence of substantially no cellulose-reactive sizing agent an anionic naphthalene sulphonate formaldehyde condensate with an aqueous alkali stabilised silica-based sol having an S-value in the range of from about 5 up to about 50% containing anionic aggregated or microgel formed

silica-based particles to provide an aqueous silica-containing composition having a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles within the range of from 0.2:1 to 99:1, and containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight.

There is further provided a method for preparation of an aqueous silica-containing composition, which comprises mixing an aqueous anionic naphthalene sulphonate formaldehyde condensate solution having a conductivity less than 20 mS/cm with an aqueous alkali stabilised sol containing silica-based particles to provide an aqueous silica-containing composition containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight.

There is further provided a method for preparation of an aqueous silica-containing composition, which comprises desalinating of an aqueous anionic naphthalene sulphonate formaldehyde condensate solution, mixing the desalinated aqueous anionic naphthalene sulphonate formaldehyde condensate solution with an aqueous alkali stabilised sol containing silica-based particles to provide an aqueous silica-containing composition containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight.

There is further provided a method for preparation of an aqueous silica-containing composition, which comprises mixing in the presence of substantially no cellulose-reactive sizing agent an anionic naphthalene sulphonate formaldehyde condensate with an aqueous alkali stabilised silica-based sol having an S-value in the range of from about 5 up to about 50% containing anionic aggregated or microgel formed silica-based particles, to provide an aqueous silica-containing composition containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight

There is further provided an aqueous silica-containing composition obtainable by the methods according to the invention.

The invention further relates to the use of the aqueous silica-containing composition of the invention, as flocculating agent in the production of pulp and paper and for water purification.

The process for the production of paper according to the present invention comprises adding to the suspension at least one cationic organic polymer and an aqueous silica-containing composition comprising anionic naphthalene sulfonate formaldehyde condensate and silica-based particles. The term "anionic naphthalene sulfonate

formaldehyde condensate" as used herein, represent a group of polymers obtained by condensation polymerisation of formaldehyde with one or more naphthalene sulphonic acids or salts thereof.

The naphthalene sulfonate formaldehyde condensate may be reacted with a base, such as alkali metal and alkaline earth hydroxides, e.g. sodium hydroxide, ammonia or an amine, e.g. triethylamine, thereby forming an alkali metal, alkaline earth or ammonium counter-ion.

The anionic naphthalene sulfonate formaldehyde condensate has a molecular weight of at least about 500, suitably from about 1,000. The upper limit is not critical it can be up to 1,000,000, usually up to 300,000, suitably up to 150,000 and preferably up to 60,000.

The aqueous silica-containing composition used in the process according to the invention also comprises anionic silica-based particles i.e. particles based on SiO_2 , preferably formed by polymerising silicic acid, encompassing both homopolymers and copolymers. Optionally the silica-based particles can be modified and contain other elements, e.g. amine, aluminium and/or boron, which can be present in the aqueous phase and/or in the silica-based particles.

Examples of suitable silica-based particles include colloidal silica, colloidal aluminium-modified silica or aluminium silicate, and different types of polysilicic acid and mixtures thereof, either alone or in combination with other types of anionic silica-based particles. In the art, polysilicic acid is also referred to as polymeric silicic acid, polysilicic acid microgel, polysilicate and polysilicate microgel, which are all encompassed by the term polysilicic acid used herein. Aluminium-containing compounds of this type are commonly referred to as polyaluminosilicate and polyaluminosilicate microgel including colloidal aluminium-modified silica and aluminium silicate.

It is preferred that the anionic silica-based particles are in the colloidal range of particle size, i.e. colloidal silica-based particles. This colloidal state comprises particles sufficiently small not to be affected by gravitational forces but sufficiently large not to show marked deviation from the properties of typical solutions, i.e. average particle size significantly less than $1\text{ }\mu\text{m}$. The anionic silica-based particles have an average particle size suitably below about 50 nm, preferably below about 20 nm and more preferably in the range of from about 1 to about 50 nm, most preferably from about 1 nm up to about 10 nm. As conventional in silica chemistry, the particle size refers to the average size of the primary particles, which may be aggregated or non-aggregated. Suitably, the silica-based particles present in the aqueous silica-containing composition of the invention comprise aggregated or microgel formed silica-based particles, optionally and usually in combination with non-aggregated, or monodisperse, silica-based particles.

Suitably the silica-based particles have a specific surface area larger than 50 m²/g, preferably larger than 100 m²/g. The specific surface area can be up to 1700 m²/g, preferably up to 1300 m²/g, and usually within the range from 300 to 1300 m²/g, preferably from 500 to 1050 m²/g. The specific surface area can be measured by means of titration
5 with NaOH according to the method described by Sears, Analytical Chemistry 28(1956), 12, 1981-1983 or in U.S. Patent No. 5,176,891. The given area thus represents the average specific surface area of the particles.

The aqueous silica-containing composition used in the process according to the invention may have a weight ratio of anionic naphthalene sulphonate formaldehyde
10 condensate to anionic silica-based particles, calculated as SiO₂, within the range of from 0.2:1 to 99:1, suitably from 0.2:1 to 90:1, preferably from 0.25:1 to 85:1. The total weight of the anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles, calculated as SiO₂, contained in the aqueous silica-containing composition is at least 0.01% by weight, calculated on the total weight of the aqueous
15 silica-containing composition, suitably the concentration of anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles, calculated as SiO₂, is within the range of 1 to 45% by weight, preferably within the range of 2 to 35 % by weight, most preferably 5 to 30% by weight.

The aqueous silica-containing composition can have an anionic charge density
20 of at least 0.1 meq/g, usually the charge is within the range of 0.1 to 6 meq/g, suitably within the range of 0.1 to 5 meq/g, preferably within the range of 0.2 to 4 meq/g, and most preferably of 0.2 to 3.5 meq/g.

The aqueous silica-containing composition according to the invention contains substantially no cellulose-reactive sizing agent. By substantially no means that less or
25 equal to 10% by weight, suitably less than 5%, preferably less than 1% by weight of cellulose-reactive sizing agent is present in the aqueous silica-containing composition. Most preferably there is no cellulose-reactive sizing agent in the aqueous silica-containing composition.

According to a preferred embodiment of the present invention, the aqueous
30 silica-containing composition contains substantially no nitrites. By substantially no means that less or equal to 10% by weight, suitably less than 5%, preferably less than 1% by weight of nitrites is present in the aqueous silica-containing composition. Most preferably there is no cellulose-reactive sizing agent in the aqueous silica-containing composition, i.e. the composition is free from nitrites. The term "nitrites" encompass all nitrites such as
35 nitrites of ammonium, lithium, kalium, sodium, calcium, and magnesium.

The present invention relates further to a method for preparation an aqueous silica-containing composition. The two components are preferably stirred together. The

anionic naphthalene sulfonate formaldehyde condensate can be added to an aqueous sol containing the silica-based particles or the silica-based particles can be added to an aqueous solution of naphthalene sulfonate formaldehyde condensate. Prior to mixing the anionic naphthalene sulfonate formaldehyde condensate with the silica-based particles, the aqueous solution of anionic naphthalene sulfonate formaldehyde condensate may be desalinated or deionised. The desalination or deionisation can be carried out with dialysis, membrane filtration, ultra-filtration, reversed osmosis or ion exchange or the like. It is preferred that the desalination or deionisation is carried out by the use of ultra-filtration or dialysis.

The anionic naphthalene sulfonate formaldehyde condensate to be mixed with the silica-based particles has the previously mentioned properties and has a conductivity less than 30 mS/cm, suitably less than 25 mS/cm, preferably less than 20 mS/cm, and most preferably less than 15 mS/cm measured at an anionic naphthalene sulfonate formaldehyde condensate content of 10%. The conductivity is usually at least 1 mS/cm, suitably at least 3 mS/cm and preferably within the range of from 5 to 15 mS/cm, measured at an anionic naphthalene sulfonate formaldehyde condensate content of 10%.

The silica-based particles, preferably anionic, to be mixed with anionic naphthalene sulfonate formaldehyde condensate have the previously mentioned properties. Suitably the silica-based particles are contained in a sol, preferably alkali stabilised, before mixing with anionic naphthalene sulfonate formaldehyde condensate. The sol may have an S-value in the range of from 5 to 50%, preferably from 8 to 45%, and most preferably from 10 to 30%. Calculation and measuring of the S-value can be performed as described by Iler & Dalton in J. Phys. Chem. 60(1956), 955-957. The S-value indicates the degree of aggregate or microgel formation and a lower S-value is indicative of a higher degree of aggregation. Suitably, the silica-based particles comprise aggregated or microgel formed silica-based particles, optionally and usually in combination with non-aggregated, or monodisperse, silica-based particles.

Suitably the silica-based particles have a molar ratio $\text{Si}_2\text{O}:\text{Na}_2\text{O}$ less than 60, usually within the range 5 to 60, and preferably within the range from 8 to 55.

The anionic naphthalene sulphonate formaldehyde condensate is usually mixed with silica-based particles in a weight ratio within a range of from 0.2:1 to 99:1, suitably from 0.2:1 to 90:1, preferably from 0.25:1 to 85:1.

The products prepared by any of these methods exhibits an improved storage stability and therefore a better drainage and retention aid performance when stored.

The mixing procedure of above mention methods is suitably carried out in the presence of substantially no cellulose-reactive sizing agent. By substantially no means

that less or equal to 10% by weight, suitably less than 5%, preferably less than 1% by weight of cellulose-reactive sizing agent is present. Most preferably there is no cellulose-reactive sizing agent present.

The present invention further relates to a process for the production of paper from an aqueous suspension containing cellulosic fibres. The process comprises adding to the suspension a cationic organic polymer and the aqueous silica-containing composition of the invention. The cationic organic polymer according to the invention can be linear, branched or cross-linked. Preferably the cationic polymer is water-soluble or water-dispersible.

Examples of suitable cationic polymers include synthetic organic polymers, e.g. step-growth polymers and chain-growth polymers, and polymers derived from natural sources, e.g. polysaccharides.

Examples of suitable cationic synthetic organic polymers include vinyl addition polymers such as acrylate- and acrylamide-based polymers, as well as cationic poly(diallyl dimethyl ammonium chloride), cationic polyethylene imines, cationic polyamines, polyamidoamines and vinylamide-based polymers, melamine-formaldehyde and urea-formaldehyde resins.

Examples of suitable polysaccharides include starches, guar gums, celluloses, chitins, chitosans, glycans, galactans, glucans, xanthan gums, pectins, mannans, dextrans, preferably starches and guar gums. Examples of suitable starches include potato, corn, wheat, tapioca, rice, waxy maize, barley, etc.

Cationic starches and cationic acrylamide-based polymers are preferred polymers according to the invention, and they can be used singly, together with each other or together with other polymers, particularly preferred are cationic starches and cationic acrylamide-based polymers having at least one aromatic group.

The cationic organic polymers can have one or more hydrophobic groups attached to them. The hydrophobic groups can be aromatic groups, groups comprising aromatic groups or non-aromatic groups, preferably the hydrophobic groups comprise aromatic groups. The hydrophobic group can be attached to a heteroatom, e.g. nitrogen or oxygen, the nitrogen optionally being charged, which heteroatom, in turn, it can be attached to the polymer backbone, for example via a chain of atoms. The hydrophobic group may have at least 2 and usually at least 3 carbon atoms, suitably from 3 to 12 and preferably from 4 to 8 carbon atoms. The hydrophobic group is suitably a hydrocarbon chain.

Suitable dosages counted as dry substance based on dry pulp and optional filler, of the cationic polymer in the system is from 0.01 to 50 kg/t (kg/tonne, "metric ton") of, preferably from 0.1 to 30 kg/t and most preferably from 1 to 15 kg/t.

Suitable dosages counted as dry substances based on dry pulp and optional filler, of the aqueous silica-containing composition defined above in the system are from

0.01 to 15 kg/t, preferably from 0.01 to 10 kg/t calculated as an anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles, and most preferably from 0.05 to 5 kg/t.

Suitable mineral fillers of conventional types may be added to the aqueous
5 cellulosic suspension according to the invention. Examples of suitable fillers include kaolin, china clay, titanium dioxide, gypsum, talc and natural and synthetic calcium carbonates such as chalk, ground marble and precipitated calcium carbonate (PCC).

Further additives that are conventional in papermaking can of course be used in
10 combination with the chemicals according to the invention, for example anionic trash catchers (ATC), wet strength agents, dry strength agents, optical brightening agents, dyes, aluminium compounds, etc. Examples of suitable aluminium compounds include alum, aluminates, aluminium chloride, aluminium nitrate, and polyaluminium compounds, such as polyaluminium chlorides, polyaluminium sulphates, polyaluminium compounds
15 containing chloride and/or sulphate ions, polyaluminium silicate sulphates, and mixtures thereof. The polyaluminium compounds may also contain other anions than chloride ions, for example anions from sulfuric acid, phosphoric acid, or organic acids such as citric acid and oxalic acid. When employing an aluminium compound in the present process, it is usually preferably to add it to the stock prior to the polymer component and micro- or nano-particulate material. Suitable addition levels of aluminium containing compounds is
20 at least 0.001 kg/t, preferably from 0.01 to 5 kg/t and more preferably from 0.05 to 1 kg/t, calculated as Al_2O_3 based on dry pulp and optional filler.

Examples of suitable anionic trash catchers include cationic polyamines, polymers or copolymers of quaternary amines, or aluminum containing compounds.

The process of this invention is used for the production of paper. The term
25 "paper", as used herein, include not only paper and the production thereof, but also other web-like products, such as for example board and paperboard, and the production thereof. The invention is particularly useful in the manufacture of paper having grammages below 150 g/m^2 , preferably below 100 g/m^2 , for example fine paper, newspaper, light weight coated paper, super calendered paper and tissue.

30 The process can be used in the production of paper from all types of stocks, both wood containing and woodfree. The different types of suspensions of cellulose-containing fibres and the suspensions should suitably contain at least 25% by weight and preferably at least 50% of weight of such fibres, based on dry substance. The suspensions comprise fibres from chemical pulp such as sulphate, sulphite and
35 organosolv pulps wood-containing or mechanical pulp such as thermomechanical pulp, chemo-thermomechanical pulp, refiner pulp and groundwood pulp, from both hardwood and softwood, and can also be based on recycled fibres, optionally from de-inked pulps, and mixtures thereof. Preferably the stock is a wood-containing stock, which have high contents of salts and therefore high conductivity.

40 The chemicals according to the present invention can be added to the

aqueous cellulosic suspension, or stock, in conventional manner and in any order. It is usually preferably to add the cationic polymer to the stock before adding the aqueous silica-containing composition, even if the opposite order of addition may be used. It is further preferred to add the cationic polymer before a shear stage, which can be selected
5 from pumping, mixing, cleaning, etc., and to add the aqueous silica-containing composition after that shear stage.

The aqueous silica-containing composition can be used as a flocculation agent in the treatment of water for the production of drinking water or as an environmental treatment of waters for instance in lakes. The composition can also be used as flocculation agent in
10 the treatment of waste water or waste sludges.

The invention is further illustrated in the following examples, which are not intended to limit the scope thereof. Parts and % relate to parts by weight and % by weight, respectively, and all solutions are aqueous, unless otherwise stated. The units are metric.

Example 1

15 Test samples of the aqueous silica-containing compositions according to the invention were prepared by mixing an aqueous solution of naphthalene sulphonate formaldehyde condensate (NSF) with a silica sol containing silica-based particles in different dosages under moderate stirring. Reference samples were also prepared under the same condition as the test samples. One sample of NSF was ultra-filtrated and the obtained
20 product (NSF I) had a concentration of 12% by weight and the samples were diluted to a concentration of 5% by weight and had a conductivity of 12 mS/cm. Another sample of NSF was dialysed and the obtained product (NSF II) had a concentration of 12% by weight and the samples were diluted to a concentration of 5% by weight and had a conductivity of 12 mS/cm. Untreated samples of NSF (NSF III) were diluted to a
25 concentration of 5% by weight and had a conductivity of 25 mS/cm. All conductivities in the Examples were measured at a concentration of 10% by weight of NSF. The silicas used in the following Examples are all defined below in Table 1.

Table 1

Silica I	Silica sol of the type described in US 5,447,604 having a molar ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of 10, specific surface area of $870 \text{ m}^2/\text{g}$, S-value of 35% and silica content of 10.0% by weight.
Silica II	Silica sol of the type described in US 5,603,805 having a molar ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of 45, specific surface area of $850 \text{ m}^2/\text{g}$, aluminium modified with sodium aluminate to a degree of 0.25% Al_2O_3 , and S-value of 20% and silica content of 8.0% by weight.
Silica III	Silica sol of the type described in US 6,083,997 having a molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$ of 17 obtained by mixing water glass having a molar ratio

SiO₂:Na₂O of 3.4, a silica content of 15% by weight with polysilicic acid (PSA), having a silica content of 6.0% by weight.

Example 2

In the following examples test samples of naphthalene sulphonate formaldehyde condensate and silica-based particles in different dosages were added to a test stock to evaluate the performance of the composition as a drainage agent. The drainage performance was evaluated by means of a Dynamic Drainage Analyser (DDA), available from Akribi, Sweden. The DDA measures the time for draining a set volume of stock through a wire when removing a plug and applying vacuum to that side of the wire opposite to the side on which the stock is present.

In the examples a cationic polymer was added to the stock before the aqueous silica-containing compositions according to the invention or the anionic reference.

Test samples prepared from mixtures of NSF II and Silica I in different ratios, which were tested on a test stock, which was a wood containing stock having a pH of 7.6, a conductivity of 5.0 mS/cm, and a consistency of 1.43 g/l. The stock was stirred in a baffled jar at a speed of 1500 rpm throughout the test.

In the tests 20 kg/t (20 kg/tonne) of cationic starch (C1), which is a cationic potato starch with a nitrogen content of 0.5%, obtained by quarternisation of native potato starch with 3-chloro-2-hydroxypropyl dimethyl benzyl ammonium chloride was added to the stock, after 30 seconds of stirring the anionic mixture was added followed by 15 seconds stirring before drainage.

As reference silica I was used. All the samples were diluted to 0.5% of solids before the tests. Ratios and results are summarised in Table 2.

Table 2

Sample	Ratio	Dewatering times (sec.) at a dosage of:		
		1 kg/t	2 kg/t	3 kg/t
silica I		26.0	23.9	20.0
NSF II + silica I	0.25:1	25.5	19.1	15.3
NSF II + silica I	0.67:1	21.6	15.5	12.5
NSF II + silica I	1:1	20.4	14.9	12.7
NSF II + silica I	1.5:1	19.3	13.8	12.3
NSF II + silica I	4:1	17.0	12.3	13.3

Example 3

Test samples were prepared from NSF II and silica II. As reference silica II was used. All the samples were diluted to 0.5% solids before the drainage evaluation, which was performed as in Example 2, with the same stock and with 20 kg/t of C1. Ratios and

results are summarised in Table 3.

Table 3

Sample	Ratio	Dewatering times (sec.) at a dosage of:		
		1 kg/t	2 kg/t	3 kg/t
silica II		25.5	22.0	18.7
NSF II + silica II	0.25:1	-	17.1	-
NSF II + silica II	0.67:1	-	14.6	-
NSF II + silica II	1:1	20.4	13.0	11.1
NSF II + silica II	1.5:1	18.6	13.2	12.1
NSF II + silica II	4:1	16.1	12.7	12.1

Example 4

- 5 Test samples were prepared from NSF I and Silica I. Silica I was used as reference. The samples were diluted to 0.5% solids and drainage tests were performed as in Example 1. To the test stock was added 20 kg/t of C1. The stock was a wood containing stock having a conductivity of 5.0 mS/cm, a consistency of 1.52 g/l and pH = 7.8. The ratios and dewatering times are summarised in Table 4.

Table 4

Sample	Ratio	Dewatering times (sec.) at a dosage of:			
		1 kg/t	2 kg/t	3 kg/t	4kg/t
silica I		34.0	29.2	25.8	24.0
NSF I + silica I	0.25:1	30.1	22.4	17.6	14.0
NSF I + silica I	0.67:1	26.9	17.7	13.3	12.2
NSF I + silica I	1:1	25.0	16.1	12.0	12.1
NSF I + silica I	1.5:1	22.1	14.6	12.5	13.0
NSF I + silica I	4:1	18.9	13.5	12.7	14.0

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Example 5

- 15 Test samples were prepared from NSF I and Silica I. Silica I was used as a reference. The preparation procedure was the same as in previous examples. The conductivity of the wood containing stock was only 0.5 mS/cm. The amount of C1 was 30 kg/t in all tests. The drainage time for cationic starch added alone was 22 seconds. The ratios and dewatering times are summarised in Table 5.

Table 5

Sample	Ratio	Dewatering times (sec.) at a dosage of:			
		1 kg/t	2 kg/t	3 kg/t	4kg/t
silica I		19.1	16.0	13.2	9.7
NSF I + silica I	0.25:1	14.3	11.6	9.4	8.5

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NSF I + silica I	0.67:1	14.3	10.0	9.2	8.2
NSF I + silica I	1:1	13.7	9.9	8.5	8.5
NSF I + silica I	1.5:1	12.2	9.9	8.7	8.6
NSF I + silica I	4:1	12.0	10.4	9.7	9.7

Example 6

The test samples were prepared from NSF I and Silica I. As reference Silica I was used. The stock was wood containing having a conductivity of 5.0 mS/cm, a consistency of 1.52 g/l and pH = 7.8. To the stock was 3 kg/t of a cationic polyacrylamide (C-PAM), which was prepared by polymerisation of acrylamide (90 mol%) and acryloxyethyl-dimethyl-benzyl ammonium chloride (10 mol%), and having a molecular weight about 6,000,000, added in the beginning of the test. After 30 seconds of stirring a compositions of NSF I and Silica I were added followed by 15 seconds of stirring before drainage. The NSF I and Silica I compositions were diluted to 0.5% solids and the C-PAM to 0.1% solids prior to addition to the stock. The ratios and dewatering times are summarised in Table 6.

Table 6

Sample	Ratio	Dewatering times (sec.) at a dosage of:	
		0.5 kg/t	1.0 kg/t
silica I		14.4	10.3
NSF I + silica I	0.25:1	11.2	8.9
NSF I + silica I	0.67:1	10.3	9.1
NSF I + silica I	1:1	10.0	9.5
NSF I + silica I	1.5:1	10.4	9.7

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Example 7

Test samples of compositions of NSF III and Silica I, and of NSF III and Silica III were prepared. A Drainage evaluation of the samples was performed as in previous Examples in a high conductivity stock with conductivity 5.0 mS/cm. C1 was added in an amount of 20 kg/t to the stock. The ratios and dewatering times are summarised in Table 7.

Table 7

Sample	Ratio	Dewatering times (sec.) at a dosage of:	
		1 kg/t	3 kg/t
NSF III + Silica III	0.077:1	34.2	21.2
NSF III + Silica III	0.15:1	31.0	18.0

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NSF III + Silica I	0.2:1	29.9	17.7
NSF III + Silica III	0.2:1	29.2	16.4
NSF III + Silica I	0.3:1	27.9	16.2
NSF III + Silica III	0.3:1	28.0	14.6

The results show that the aqueous silica-containing composition according to the invention have improved drainage properties.

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Example 8

Test samples of compositions of NSF I and Silica I, and of NSF III and Silica III were prepared. As reference Silica I and Silica III were used. A drainage evaluation of the samples was performed as in previous Examples in a high conductivity stock with conductivity 5.0 mS/cm. C1 was added in an amount of 20 kg/t to the stock. The dewatering times summarised in Table 8.

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Table 8

Sample	Ratio	Dewatering times (sec.) at a dosage of:	
		2 kg/t	3 kg/t
Silica I		27.2	24.3
Silica III		26.8	20.9
NSF III + Silica III	0.077:1	27.3	21.2
NSF III + Silica III	0.15:1	23.1	18.0
NSF I + Silica I	0.2:1	21.4	15.8
NSF I + Silica I	0.3:1	20.7	15.1
NSF III + Silica III	0.2:1	20.7	16.4
NSF III + Silica III	0.3:1	20.2	14.6

The results show that the aqueous silica-containing compositions according to the invention have improved drainage properties.

Example 9

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A high molecular weight anionic polyacrylamide (A-PAM), MW from about 10 to 20 millions, containing about 30 mole-% anionic groups, in form of a water-in-oil emulsion inverted and diluted with water to a concentration of 0.1 %. The A-PAM was mixed with 0.1% of Silica I in three different ratios of A-PAM to Silica I of 2:1, 1:1 and 0.5:1.

Compositions of NSF III and Silica III (a) was prepared by adding a diluted water glass (15% SiO₂ and ratio SiO₂/Na₂O = 3.4) to NSF III (as 30% water solution) under agitation. To this mixture was polysilicic acid, with a concentration of 6.0 % SiO₂ a pH of 2.5, added under agitation for 20 minutes. The polysilicic acid was prepared from diluted waterglass that was run through a column filed with hydrogen saturated, strongly cationic, ion exchange resin.

NSF III/Silica III (b) mixture was prepared mixing NSF III with polysilicic acid under agitation for 5 minutes and then this mixture was added to waterglass under agitation for 20 minutes.

A drainage evaluation of the samples of this example were performed on a high conductivity stock (5.0 m S/cm). A cationic starch (C2), which was a cationic potato starch with a nitrogen content of 0.7%, obtained by quaternisation of native potato starch with 3-chloro-2-hydroxypropyl dimethyl benzyl ammonium chloride, was added before the anionic mixtures to the stock. C2 was added in an amount of 12kg/t. The following dewatering times were obtained:

Table 9

Sample	Ratio	Dewatering times (sec.) at a dosage of
		2.0 kg/t
A- PAM		33.0
Silica I		16.9
A-PAM / Silica I	0.5:1	28.7
A-PAM / Silica I	1:1	25.5
A-PAM / Silica I	2:1	29.4
NSF III / Silica III a	0.38:1	22.0
NSF III / Silica III a	1.9:1	21.0
NSF III / Silica III a	9:1	17.7
NSF III / Silica III b	0.5:1	23.0
NSF III / Silica III b	9:1	16.8

Example 10

The storage stability of different mixtures of NSF and silica were determined. Samples of NSF was desalinated by the use of ultrafiltration (NSF I) to a conductivity of 12 mS/cm measured at 10% by weight of solids before mixing with silica to form aqueous compositions. Untreated NSF III were mixed with silica for comparison.

All obtained aqueous compositions and the reference samples were stored according to the following procedure:

In a refrigerator for 9 weeks; then

in oven at a temperature of 40°C for 3 weeks;

5 in oven at a temperature of 60°C for 1 week; and

in oven at a temperature of 80°C for 6 weeks.

The total storage time was 20 weeks. The storage times for the test samples are summarised in Table 10.

Table 10

Sample	Ratio	Active substance (SiO ₂ + NSF)	Time of gel formation
NSF III + Silica III	0.15:1	7.2%	gel after 14 weeks
NSF I + Silica III	0.15:1	7.2%	no gel after 20 weeks
NSF I + Silica III	0.2:1	7.3%	no gel after 20 weeks

10 The samples with no gel formation show better stability than the samples with gel-formation, and they did not even show an increase in viscosity.

Example 11

15 Test samples of mixtures of NSF III / Silica I and of mixtures of NSF III / Silica III were prepared. As reference Silica III was used. A DDA evaluation of the samples was performed in a high conductivity stock with conductivity 5.0 mS/cm. C1 was added in an amount of 20 kg/t to the stock. The dewatering times summarised in Table 11.

Table 11

Sample	Dewatering times (seconds) 1 kg/t
Silica sol III	32.1
Silica sol III with 7.7% NSF III	34.2
Silica sol I with 7.7% NSF III	29.4
Silica sol III with 15% NSF III	31.0
Silica sol I with 15% NSF III	30.7

20 The results show that the mixtures containing Silica I have received improved dewatering times compared to Silica III. Silica I is an alkali stabilised silica sol.

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Claims

1. A process for the production of paper from a suspension containing cellulosic fibres, and optionally fillers, comprising adding to the suspension at least one cationic organic polymer and an aqueous silica-containing composition comprising an anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles, the composition having a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles, calculated as SiO_2 , within the range of from 0.2:1 to 99:1, and containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight, based on the total weight of the aqueous silica-containing composition, and with the proviso that the composition contains substantially no cellulose-reactive sizing agent.
2. The process according to claim 1, wherein the anionic silica-based particles comprise aggregated or microgel formed silica-based particles.
3. The process according to claim 1 or 2, wherein the anionic naphthalene sulphonate formaldehyde condensate has a conductivity of less than 20 mS/cm.
4. The process according to claim 3, wherein the anionic naphthalene sulphonate formaldehyde condensate has a conductivity of less than 15 mS/cm.
5. The process according to any of the preceding claims, wherein the aqueous silica-containing composition has a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles, calculated as SiO_2 , within the range of from 0.2:1 to 90:1.
6. The process according to any of the preceding claims, wherein the anionic silica-based particles have a specific surface area within the range of from 300 to 1300 m^2/g .
7. The process according to any of the preceding claims, wherein the cationic organic polymer is cationic starch or cationic polyacrylamide.
8. The process according to any of the preceding claims, wherein the cationic organic polymer has at least one aromatic group.

9. Use of an aqueous silica-containing composition according to any of claims 1 to 8, as a flocculating agent in the production of pulp and paper and for water purification.

10. An aqueous silica-containing composition comprising an anionic naphthalene sulphonate formaldehyde condensate and anionic silica-based particles comprising aggregated or microgel formed silica-based particles, the composition having a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles, calculated as SiO_2 , within the range of from 0.2:1 to 99:1, and containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight, based on the total weight of the aqueous silica-containing composition, and with the proviso that the composition contains substantially no cellulose-reactive sizing agent.

11. An aqueous silica-containing composition obtainable by mixing anionic naphthalene sulphonate formaldehyde condensate with an aqueous alkali stabilised silica-based sol having an S-value in the range of from about 5 up to about 50% containing anionic aggregated or microgel formed silica-based particles, to provide an aqueous silica-containing composition containing an anionic naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight, based on the total weight of the aqueous silica-containing composition, with the proviso that the aqueous silica-containing composition contains substantially no cellulose-reactive sizing agent.

12. The aqueous silica-containing composition according to claim 10 or 11, wherein the anionic naphthalene sulphonate formaldehyde condensate has a conductivity of less than 15 mS/cm.

13. The aqueous silica-containing composition according to claim 10 or 11, wherein the aqueous silica-containing composition has a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles, calculated as SiO_2 , within the range of from 0.2:1 to 90:1.

14. The aqueous silica-containing composition according to claim 10 or 11, wherein the silica-based particles have a specific surface area within the range of from 300 to 1300 m^2/g .

15. A method for preparation of an aqueous silica-containing composition, which comprises mixing in the presence of substantially no cellulose-reactive sizing agent an anionic naphthalene sulphonate formaldehyde condensate with an aqueous alkali stabilised silica-based sol having an S-value in the range of from about 5 up to about 50% containing anionic aggregated or microgel formed silica-based particles to provide an aqueous silica-containing composition having a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles, calculated as SiO_2 , within the range of from 0.2:1 to 99:1, and containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight.
16. A method for preparation of an aqueous silica-containing composition, which comprises mixing an aqueous anionic naphthalene sulphonate formaldehyde condensate solution having a conductivity less than 20 mS/cm with an aqueous alkali stabilised sol containing silica-based particles to provide an aqueous silica-containing composition containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight.
17. A method for preparation of an aqueous silica-containing composition, which comprises desalinating of an aqueous anionic naphthalene sulphonate formaldehyde condensate solution, mixing the desalinated aqueous anionic naphthalene sulphonate formaldehyde condensate solution with an aqueous alkali stabilised sol containing silica-based particles to provide an aqueous silica-containing composition containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight.
18. A method for preparation of an aqueous silica-containing composition, which comprises mixing in the presence of substantially no cellulose-reactive sizing agent an anionic naphthalene sulphonate formaldehyde condensate with an aqueous alkali stabilised silica-based sol having an S-value in the range of from about 5 up to about 50% containing anionic aggregated or microgel formed silica-based particles, to provide an aqueous silica-containing composition containing naphthalene sulphonate formaldehyde condensate and silica-based particles, calculated as SiO_2 , in an amount of at least 0.01 % by weight.

19. The method according to claims 15, 16, 17 or 18, wherein the anionic naphthalene sulphonate formaldehyde condensate has a conductivity of less than 15 mS/cm.
- 5 20. The method according to claims 15, 16, 17 or 18, wherein the aqueous silica-containing composition has a weight ratio of naphthalene sulphonate formaldehyde condensate to silica-based particles, calculated as SiO_2 , within the range of from 0.2:1 to 90:1.
- 10 21. The method according to claims 15, 16, 17 or 18, wherein the silica-based particles have a specific surface area within the range of from 300 to 1300 m^2/g .
22. The method according to claims 16 or 17, wherein the sol has an S-value within the range of from 5 to 50% prior to mixing with the anionic of naphthalene sulphonate
15 formaldehyde condensate.
23. The method according to claims 15, 16, 17 or 18, wherein the sol has an S-value within the range of from 8 to 45% prior to mixing with the anionic of naphthalene sulphonate formaldehyde condensate.

INTERNATIONAL SEARCH REPORT

International App. No.
PCT/SE 02/02443

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D21H17/71 D21H17/68 D21H21/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 443 496 A (OBITSU MASAMICHI ET AL) 17 April 1984 (1984-04-17) claims 1-8	10, 15-18
X	US 4 559 241 A (OBITSU MASAMICHI ET AL) 17 December 1985 (1985-12-17) claims 1,2	10, 15-18
Y	US 5 595 629 A (BEGALA ARTHUR J) 21 January 1997 (1997-01-21) claims 1-10; examples 1-5; table 1	1, 10, 15-18
Y	EP 0 418 015 A (ALBRIGHT & WILSON) 20 March 1991 (1991-03-20) cited in the application claims 1-15; examples 17-19	1, 10, 15-18
	--- -/-	

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Date of the actual completion of the international search

17 April 2003

Date of mailing of the international search report

08/05/2003

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PCT/SE 02/02443

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 033 524 A (JAKUBOWSKI REGINA ET AL) 7 March 2000 (2000-03-07) claims 1-18	1,10, 15-18
A	US 6 165 259 A (FROELICH STEN ET AL) 26 December 2000 (2000-12-26) the whole document	1-23
A	US 4 070 236 A (CARRARD JEAN-PIERRE ET AL) 24 January 1978 (1978-01-24) the whole document	1-23
A	US 4 772 332 A (NEMEH SAAD ET AL) 20 September 1988 (1988-09-20) the whole document	1-23
A	GB 2 294 708 A (CIBA GEIGY AG) 8 May 1996 (1996-05-08) the whole document	1-23
A	US 5 733 414 A (STOCKWELL JOHN OLIVER) 31 March 1998 (1998-03-31) the whole document	1-23
A	US 5 110 414 A (FUHRMANN AGNETA G M ET AL) 5 May 1992 (1992-05-05) the whole document	1-23

INTERNATIONAL SEARCH REPORT
Information on patent family members

International App. No.
PCT/SE 02/02443

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4443496	A	17-04-1984	JP 1301472 C	14-02-1986
			JP 58020768 A	07-02-1983
			JP 59024759 B	12-06-1984
			DE 3266831 D1	14-11-1985
			EP 0072138 A2	16-02-1983
			US 4521249 A	04-06-1985
US 4559241	A	17-12-1985	JP 1473030 C	27-12-1988
			JP 60108385 A	13-06-1985
			JP 63020799 B	30-04-1988
			AU 574398 B2	07-07-1988
			AU 3512184 A	16-05-1985
			DE 3466870 D1	26-11-1987
			EP 0147043 A1	03-07-1985
US 5595629	A	21-01-1997	BR 9603843 A	02-06-1998
			CA 2182073 A1	23-03-1997
			DE 19632079 A1	27-03-1997
			FR 2739110 A1	28-03-1997
EP 0418015	A	20-03-1991	AU 6231790 A	14-03-1991
			BR 9004518 A	10-09-1991
			CA 2024975 A1	12-03-1991
			EP 0418015 A1	20-03-1991
			JP 3167391 A	19-07-1991
			NO 903926 A	12-03-1991
			ZA 9007216 A	31-07-1991
US 6033524	A	07-03-2000	WO 0049227 A1	24-08-2000
			AU 4223299 A	04-09-2000
			CA 2315676 A1	28-11-2000
			EP 1104495 A1	06-06-2001
			JP 2002537498 T	05-11-2002
			NZ 505246 A	28-03-2002
US 6165259	A	26-12-2000	AT 225437 T	15-10-2002
			AT 225436 T	15-10-2002
			AT 225435 T	15-10-2002
			AU 729667 B2	08-02-2001
			AU 6009998 A	25-08-1998
			AU 729833 B2	08-02-2001
			AU 6010098 A	25-08-1998
			AU 729702 B2	08-02-2001
			AU 6010198 A	25-08-1998
			BR 9807040 A	28-03-2000
			BR 9807049 A	28-03-2000
			BR 9807978 A	15-02-2000
			CN 1280640 T	17-01-2001
			CN 1246899 T	08-03-2000
			CN 1246900 T	08-03-2000
			DE 69808435 D1	07-11-2002
			DE 69808436 D1	07-11-2002
			DE 69808437 D1	07-11-2002
			DK 963484 T3	20-01-2003
			DK 961855 T3	20-01-2003
			EP 0963485 A2	15-12-1999
			EP 0963484 A1	15-12-1999
			EP 0961855 A1	08-12-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Publication No

PCT/SE 02/02443

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6165259	A	ES 2183323 T3	16-03-2003
		ES 2183324 T3	16-03-2003
		ES 2183325 T3	16-03-2003
		JP 3268582 B2	25-03-2002
		JP 2000509447 T	25-07-2000
		JP 3175774 B2	11-06-2001
		JP 2000509448 T	25-07-2000
		JP 2000509430 T	25-07-2000
		NO 993740 A	28-09-1999
		NO 993741 A	27-09-1999
		NO 993742 A	29-09-1999
		NZ 336572 A	26-01-2001
		NZ 336786 A	23-02-2001
		NZ 336787 A	28-04-2000
		PT 963484 T	31-01-2003
		PT 961855 T	31-01-2003
		SK 102599 A3	14-08-2000
		SK 103099 A3	16-05-2000
		US 5969011 A	19-10-1999
		US 6093217 A	25-07-2000
		US 6306255 B1	23-10-2001
		RU 2168579 C2	10-06-2001
		WO 9833980 A1	06-08-1998
		WO 9833979 A1	06-08-1998
US 4070236	A	24-01-1978 CH 586321 A5	31-03-1977
		CH 587962 A5	31-05-1977
		DE 2549089 A1	26-05-1976
		FI 753114 A	16-05-1976
		GB 1525110 A	20-09-1978
		JP 51070301 A	17-06-1976
US 4772332	A	20-09-1988 SE 7512462 A	17-05-1976
		AT 85066 T	15-02-1993
		AU 2873589 A	27-07-1989
		BR 8900287 A	19-09-1989
		CA 1319583 A1	29-06-1993
		CN 1034944 A	23-08-1989
		DE 3877940 D1	11-03-1993
		DE 3877940 T2	19-08-1993
		EP 0325852 A2	02-08-1989
		FI 890344 A	26-07-1989
		JP 2003453 A	09-01-1990
		AT 76655 T	15-06-1992
		AU 606931 B2	21-02-1991
		AU 1414988 A	20-10-1988
		BR 8801870 A	22-11-1988
		CN 88102312 A , B	07-12-1988
		DE 3871432 D1	02-07-1992
		EP 0288291 A2	26-10-1988
		ES 2032961 T3	01-03-1993
		FI 881800 A	22-10-1988
		JP 63278986 A	16-11-1988
		KR 9603934 B1	23-03-1996
		US 4859246 A	22-08-1989
GB 2294708	A	08-05-1996 DE 69522172 D1	20-09-2001
		DE 69522172 T2	29-05-2002

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
PCT/SE 02/02443

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2294708	A		EP 0712960 A1	22-05-1996
			ES 2161851 T3	16-12-2001
			JP 8209013 A	13-08-1996
			US 5830241 A	03-11-1998
US 5733414	A	31-03-1998	AT 193915 T	15-06-2000
			AU 701218 B2	21-01-1999
			AU 1583095 A	21-08-1995
			BR 9505837 A	27-02-1996
			CA 2159592 A1	10-08-1995
			DE 69517474 D1	20-07-2000
			DE 69517474 T2	08-03-2001
			DK 695385 T3	30-10-2000
			EP 0695385 A1	07-02-1996
			ES 2149346 T3	01-11-2000
			FI 954676 A	02-10-1995
			WO 9521295 A1	10-08-1995
			JP 8508795 T	17-09-1996
			NO 953935 A	03-10-1995
			NZ 279257 A	27-05-1998
			PL 310978 A1	22-01-1996
			ZA 9500923 A	06-02-1996
US 5110414	A	05-05-1992	FI 871010 A	10-09-1988
			AT 125191 T	15-08-1995
			AU 607259 B2	28-02-1991
			AU 2205588 A	21-06-1990
			CA 1288204 A1	03-09-1991
			DE 3854193 D1	24-08-1995
			DE 3854193 T2	14-12-1995
			DK 619888 A	07-11-1988
			EP 0355094 A1	28-02-1990
			ES 2006106 A6	01-04-1989
			WO 8807104 A1	22-09-1988
			GR 88100142 A ,B	31-01-1989
			NO 884973 A ,B,	06-01-1989